COURSE ON ULTRAFINE PARTICLES AND RETROFIT DIESEL ENGINES Johnson Matthey

DIAMOND BAR, CA, NOVEMBER 12, 2008

CATALYTIC COATINGS FOR DIESEL PARTICULATE FILTER REGENERATION

Dr. Claus Görsmann
HDD OE Non-Road and Retrofit Technology Manager



Catalysts

CONTENTS



- Introduction catalytic coatings
- Regeneration of Diesel particulate filter systems
 - Oxygen and NO₂ based soot oxidation
 - Passive systems (NO₂ based, e.g. CRT[®], CSF, CCRT[®])
 - Active systems (O₂ based, e.g. ACRT[®])
- Strategies for DPF systems with low NO₂ emissions
 - Low-NO₂ CRT[®] system
 - SCRT® retrofit systems: the most complete diesel emission control
- Conclusions

CATALYTIC COATINGS... (1/2)



- Are a well proven and an essential part of Otto- and Dieselengine exhaust aftertreatment systems
- Are used to clean-up Diesel emissions in
 - Millions of Diesel oxidation catalysts (standard in today's Diesel engine powered passenger cars)
 - Millions of Diesel engine powered passenger car soot filter systems
 - Hundreds of thousands of HDD soot filter systems
 - The vast majority of HDD retrofit soot filter systems

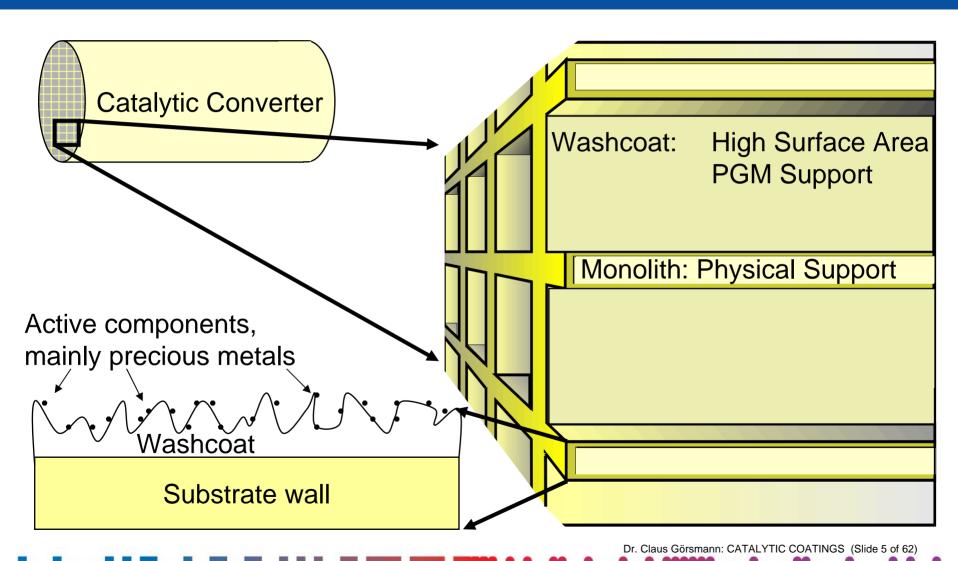
CATALYTIC COATINGS... (2/2)



- Are applied to surfaces within the exhaust aftertreatment system, mainly purpose-made substrates (flow through monoliths or wall flow filters).
 - Catalyst substrates typically consist of either Cordierite- or metal supports
 - Filter substrates are typically made of Silicon carbide (SiC),
 Cordierite or sintered metal
- Consist of active components (mainly precious metals) and components (mainly non precious metal oxides), which enhance the efficiency and stability of the active components. These components are called "washcoat".

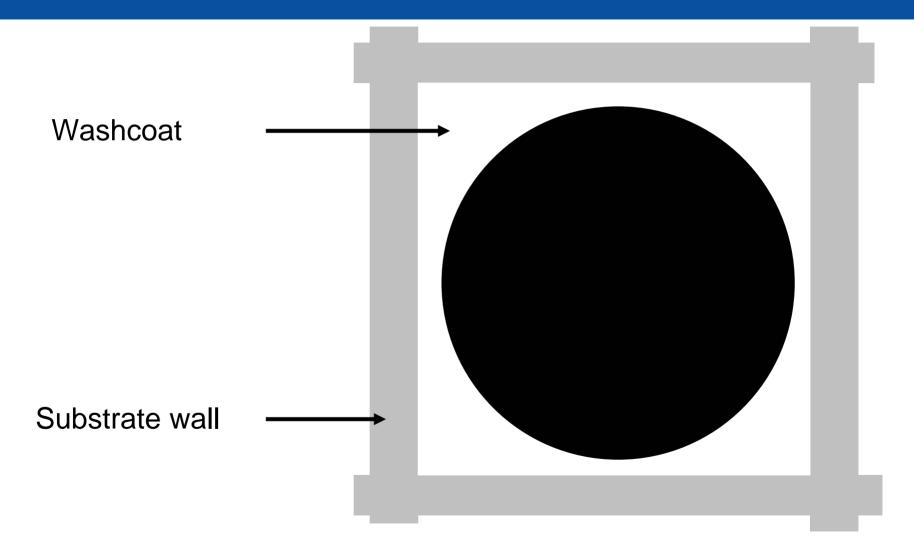
STRUCTURE OF A CATALYTIC CONVERTER





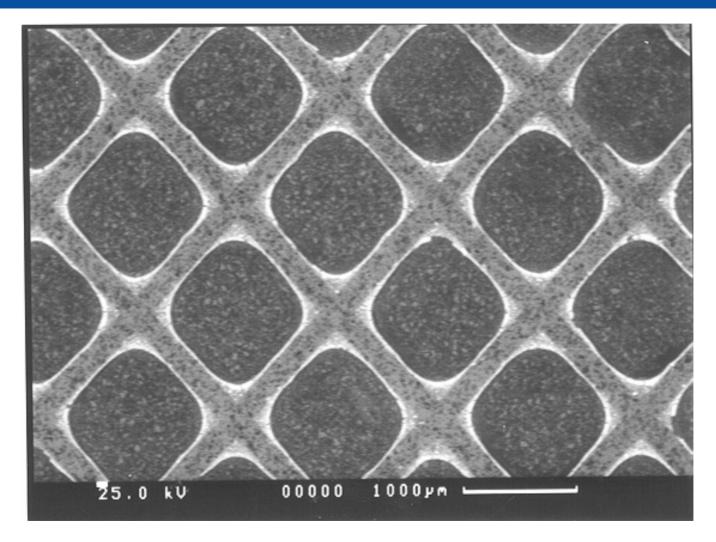
SCHEMATIC: CHANNEL IN CATALYST (AXIAL VIEW)





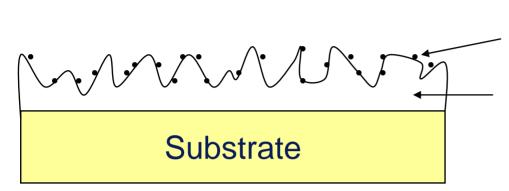
SEM IMAGE OF COATED SUBSTRATE





TYPICAL DATA FOR CATALYTIC COATINGS





Active components, mainly precious metals Washcoat

- Typical...
 - Specific surface are of the substrate: 0.1-1m²/g
 - Specific surface area of washcoat: 50-500m²/g
 - Washcoat loading: 20-200g/litre catalyst volume
 - Washcoat thickness: 0.01-0.2mm
 - Loading of active components: 0.01-10g/litre catalyst volume

GENERAL REQUIREMENTS FOR CATALYTIC COATINGS



- High catalytic activity (and sometimes also high selectivity e.g. for SCR catalysts)
- High chemical and thermal stability
- Minimal influence on exhaust backpressure (especially for coatings on filter)

The means to meet these targets are contradictory and require compromises in order to achieve application optimised systems.

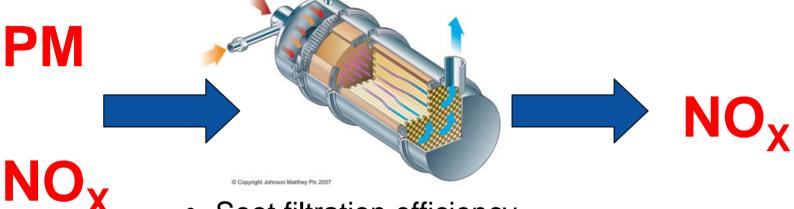
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PM CONTROL: DIESEL PARTICULATE FILTER SYSTEMS





- Soot filtration efficiency
 - Partial filtration
 - Full filtration
- Regeneration
 - Passive (NO₂ based)
 - Active (O₂ or NO₂ based)
 - Burner Systems

REGENERATION OF DIESEL PARTICULATE FILTER SYSTEMS: FORMING OF GASEOUS PRODUCTS



Evaporation and Decomposition trough heat

$$\bullet \ \ \mathsf{H}_2\mathsf{O}(\mathsf{I}) \to \mathsf{H}_2\mathsf{O}(\mathsf{g}) \tag{1}$$

•
$$H_2SO_4 \rightarrow SO_2 + H_2O + \frac{1}{2}O_2$$
 (2)

•
$$2 \text{ HNO}_3 \rightarrow 2 \text{ NO}_2 + \text{H}_2\text{O} + \frac{1}{2} \text{ O}_2$$
 (3)

Oxidation of soot through Oxygen via O2 or NO2

$$\bullet C + 2 "O" \rightarrow CO_2$$
 (4)

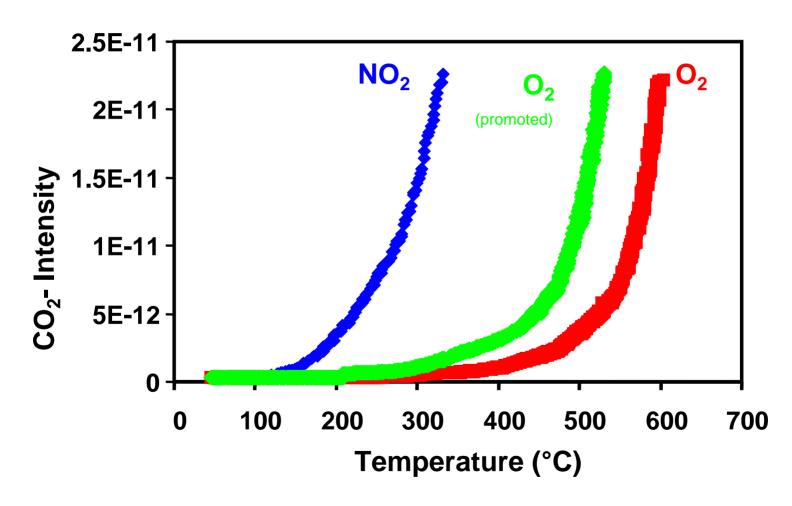
$$\bullet C + O_2 \longrightarrow CO_2 \tag{4a}$$

•
$$C + 2 NO_2 \rightarrow CO_2 + 2 NO$$
 (4b)

•
$$C_X H_Y + (2x+y/2) "O" \rightarrow x CO2 + y/2 H_2O$$
 (5)

SOOT COMBUSTION (TO CO₂) BY NO₂ AND O₂ AS A FUNCTION OF TEMPERATURE





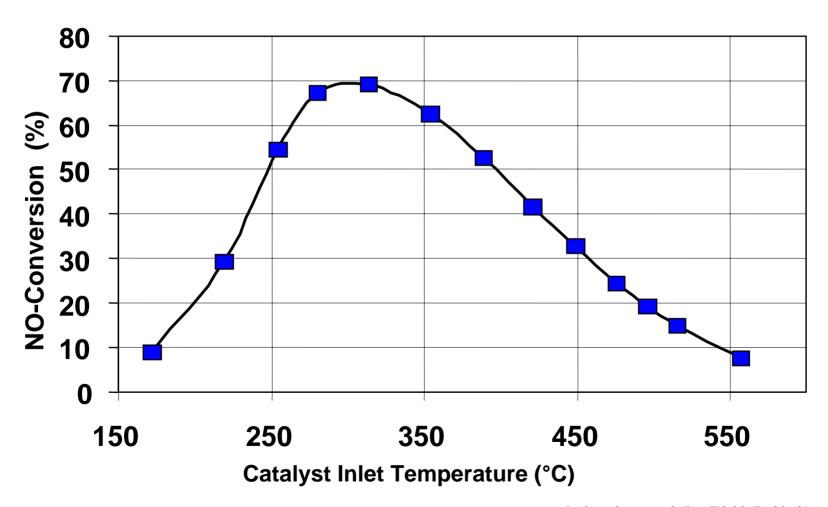
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NO CONVERSION TO NO₂ OVER A DOC

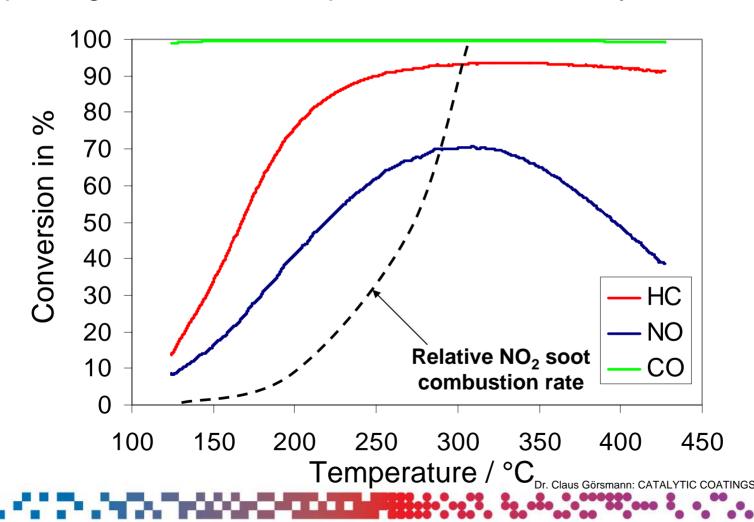




PASSIVE DOC PERFORMANCE

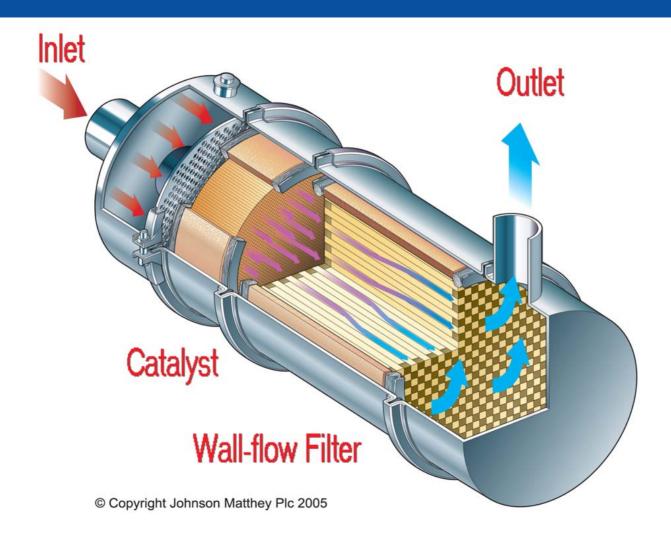


Typical light-off conversion profile for a DOC catalyst



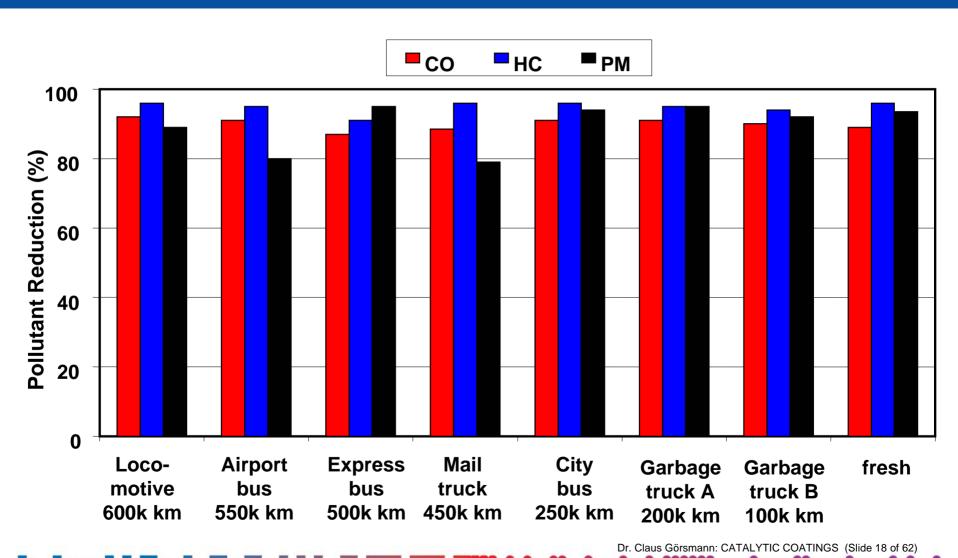
CRT® SCHEMATIC DRAWING





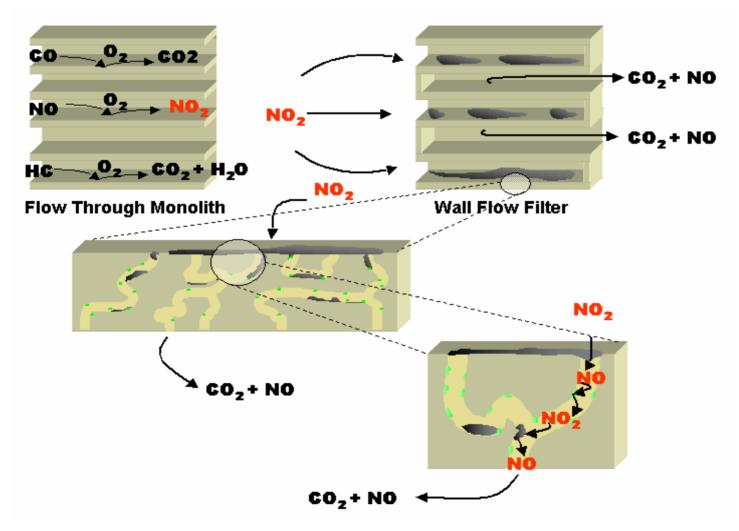
FIELD EXPERIENCE CRT® - POLLUTANT REDUCTION





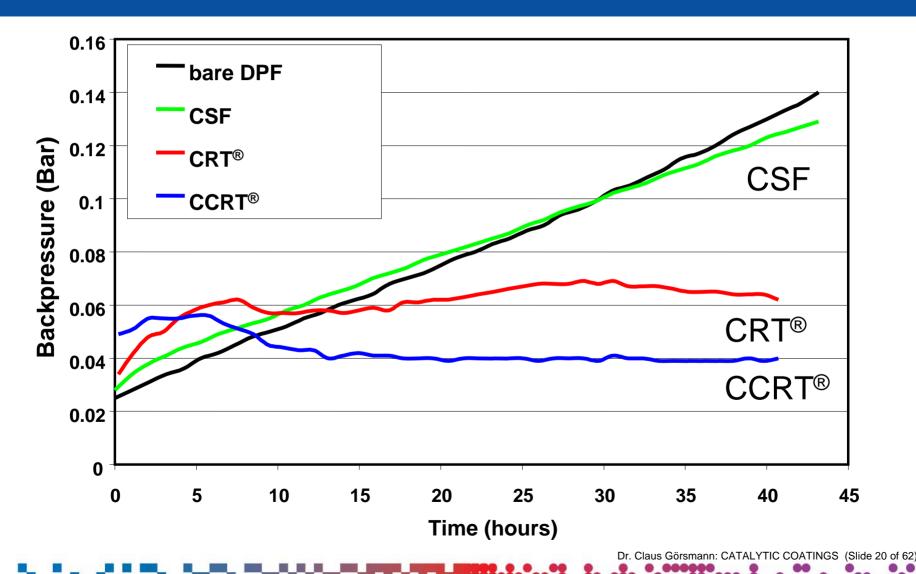
PRINCIPLE CRT®, CSF AND CCRT®





PERFORMANCE OVER LOW TEMPERATURE CYCLE (T < 270°C)





EXPERIENCE FROM ON-ROAD SYSTEMS



- Europe (EU IV and EU V)
 - SCR: total market so far ca. 450,000
 - EGR + DOC (+ partial DPF): total market so far ca. 200,000
- USA (EPA 2007): total market so far ca. 375,000
 - DOC + CSF
 - Burner + CSF
- Systems under development to meet future Japanese (JP09), US (EPA 2010) and European (EU VI) legislation will combine PM control with NOx aftertreatment.
- Non-road emissions aftertreatment systems can benefit from the experience from on-road applications.

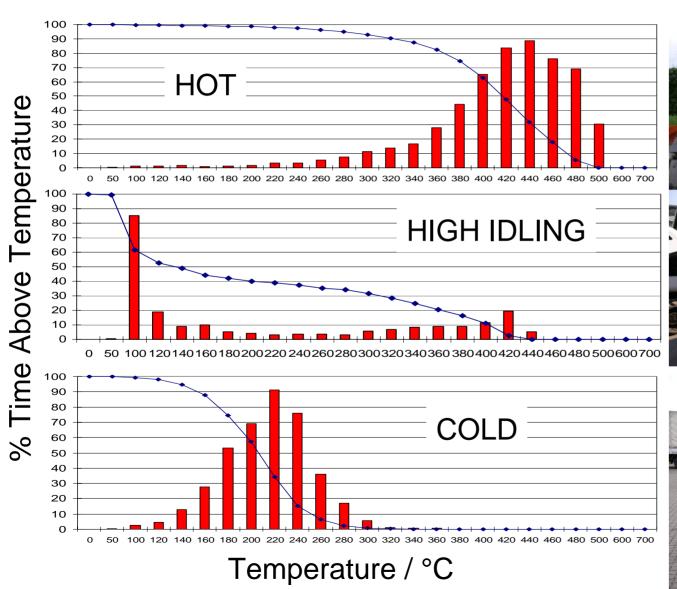
DPF-SYSTEMS RETROFIT EXPERIENCE



- Of the 150,000 HDD vehicles retrofitted with JM DPF systems globally, there are several thousand non-road machines in Europe (mainly Switzerland) and USA.
- By far the most successful non-road retrofit systems are the purely passive systems CRT[®] (DOC+DPF) and CCRT[®] (DOC + coated DPF).
- Electrically regenerating systems ("DPFi") have been applied in combination with a CRT® or fuel borne catalyst in applications, which are not suitable for passive regeneration (too cold and/or unfavorable NO_x/PM ratio or too dirty).

EXAMPLES FOR VERY DIFFERENT DUTY CYCLES









EXAMPLES: CRT® ON NON-ROAD EQUIPMENT









CAT 657 E Scraper Retrofit



CASE MX100 Tractor



CAT 966 G2 Excavator

Dr. Claus Görsmann: CATALYTIC COATINGS (Slide 24 of 62)

EXAMPLE: CRT® SYSTEM ON TRACTOR





Dr. Claus Görsmann: CATALYTIC COATINGS (Slide 25 of 62)

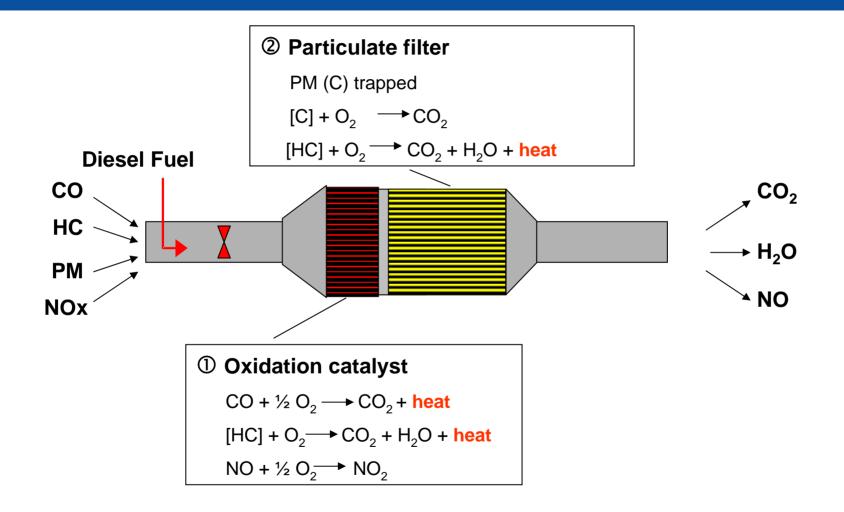
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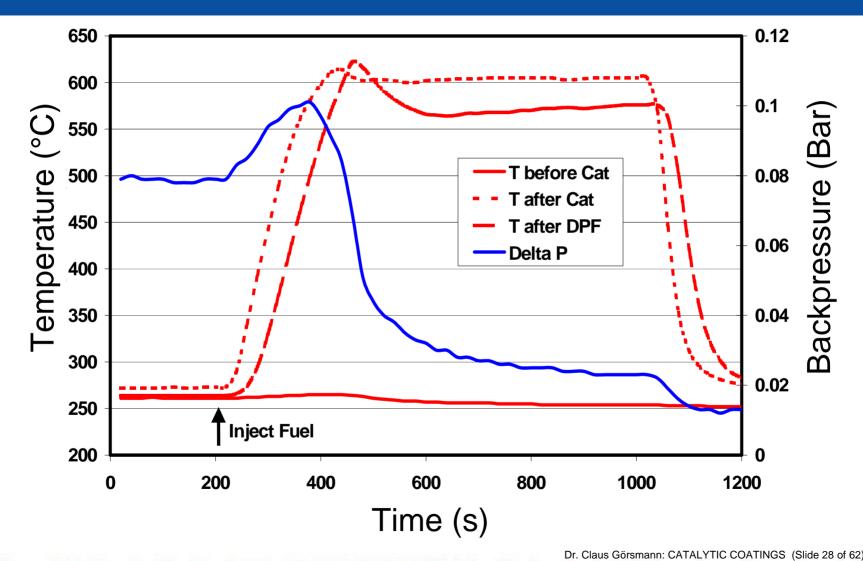
PRINCIPLE OF ACTIVE REGENERATION UTILISING CATALYTIC COMBUSTION





ACTIVE REGENERATION OF A CRT® WITH O₂ (105 g SOOT ON 17-LITRE DPF)

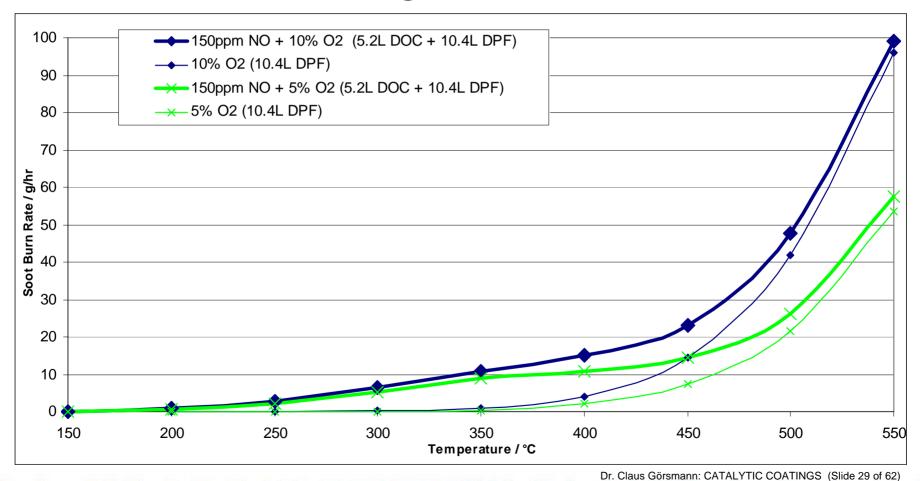




SOOT COMBUSTION - NO2 CONTRIBUTION

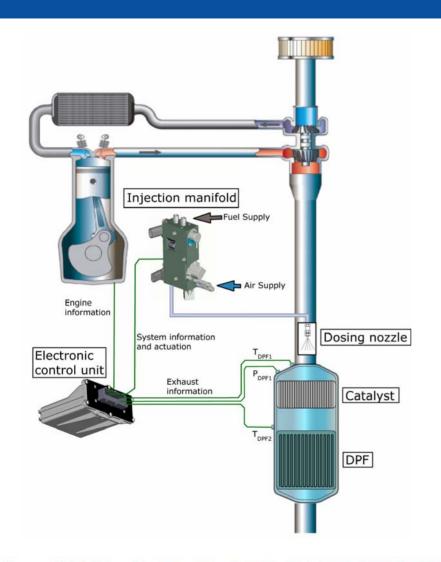


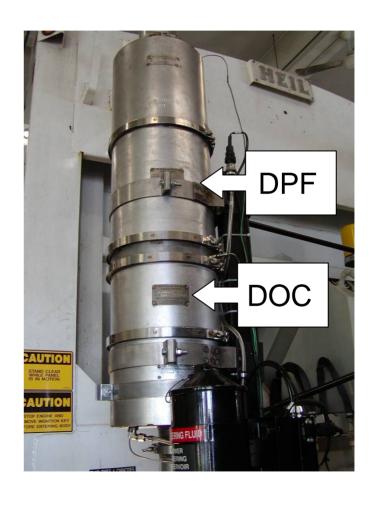
Exhaust Mass Flow = 450 kg/hr



ACTIVE REGENERATION WITH FUEL INJECTION - ACRT™ SYSTEM







Dr. Claus Görsmann: CATALYTIC COATINGS (Slide 30 of 62)

ACTIVE REGENERATION WITH FUEL INJECTION – NY DOS TRUCK





CHALLENGES FOR PASSIVE AND ACTIVE SYSTEMS



Passive (NO₂ based) systems

- Temperature profile
- NO_X/PM ratio
- Ultra low sulphur fuel (max. 50ppm S) required

Active (O₂ based) systems

- Soot loading, trigger regeneration
- Temperature control during transient operation
- Fuel injection
- O₂ control
- Heat dissipation

ACTIVE (O₂-BASED) REGENERATION THROUGH BURNER SYSTEM OR CATALYTIC FUEL COMBUSTION



(Full flow) burner system

- High flexibility for regeneration
- Very complex hardware
 - Burner (can be bulky)
 - Air supply
 - Very sophisticated control
- Limited passive regeneration
 - More frequent regeneration required (higher fuel penalty)

Catalytic fuel combustion

- Requires minimum exhaust temperature (≈250°C) to initiate regeneration
- Less complex hardware
 - Fuel injector
- Uses Common rail capabilities or seperate fuel injector
- Uses exhaust gas as O₂ source
- Can be easily combined with passive regeneration (lower backpressure and fuel penalty)
- More compact
- Most popular US-2007 on-road PM control solution.

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FACTORS, WHICH INFLUENCE NO₂ EMISSIONS



- Engine raw emissions
 - NO_x
 - PM
- Catalyst / Filter
 - Size
 - Formulation
 - Ageing
- Temperature
- DPF Soot loading

HOW CAN NO₂ EMISSIONS FROM CRT®s BE MINIMISED?



- → Avoiding NO₂-Formation
- → Removing NO₂ downstream of the DPF

HOW CAN NO₂ EMISSIONS FROM CRT[®]s BE MINIMISED?



- AVOIDING NO₂-FORMATION
- Minimising of NO_x upstream of the DOC
 - EGR: EGRT®
 - SCR
 - NOx-adsorber catalyst
 - All these technologies have a negative impact on the CRT[®] function
- Controlling the NO₂ formation of the DOC
 - DOC optimisation
 - Sizing
 - Metal loading
 - Formulation

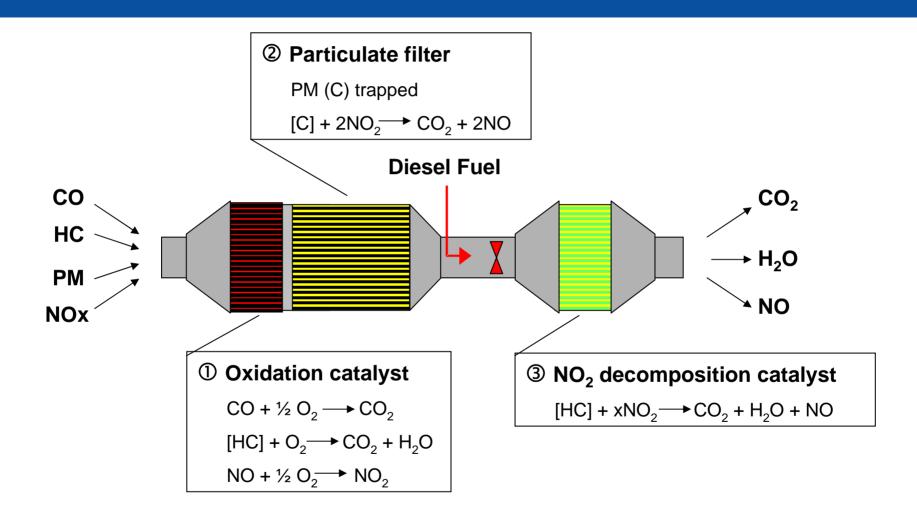
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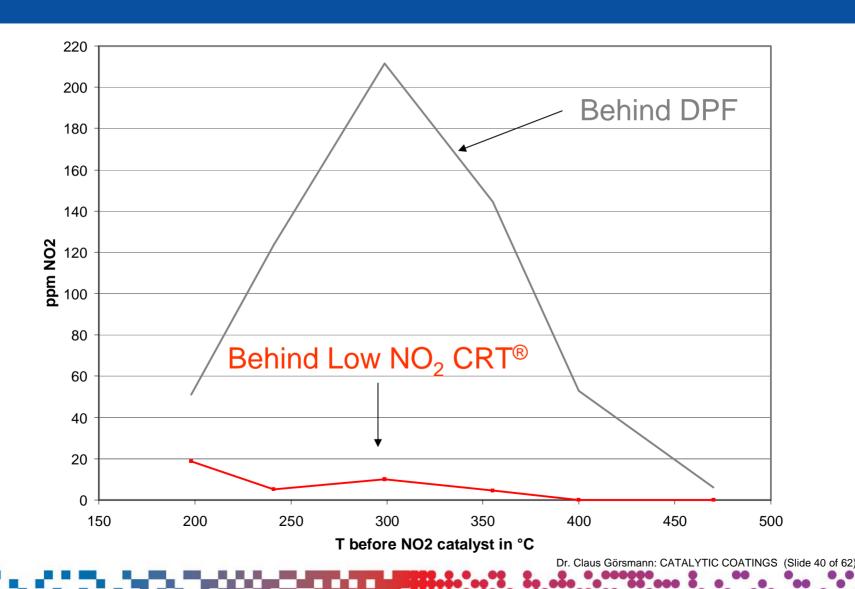
THE LOW NO, CRT® SYSTEM





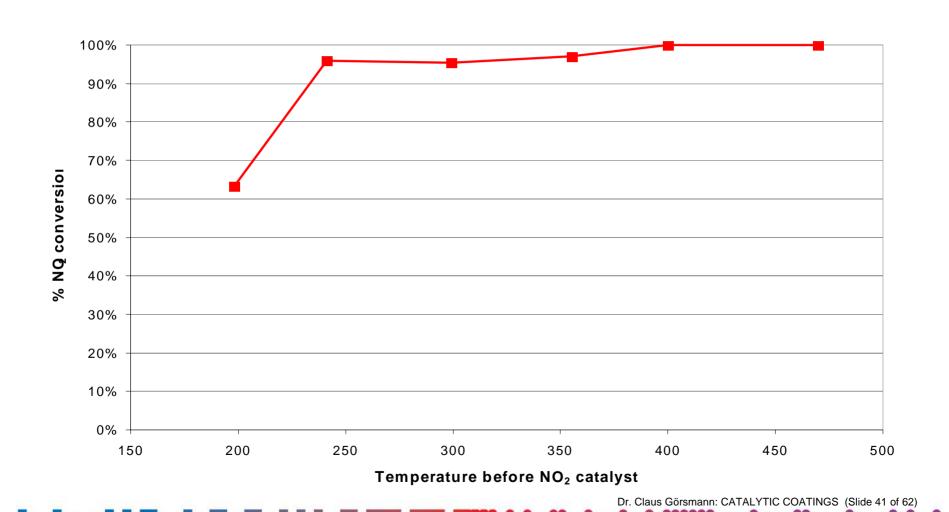
NO₂ CONCENTRATION BEHIND A LOW NO₂ CRT®





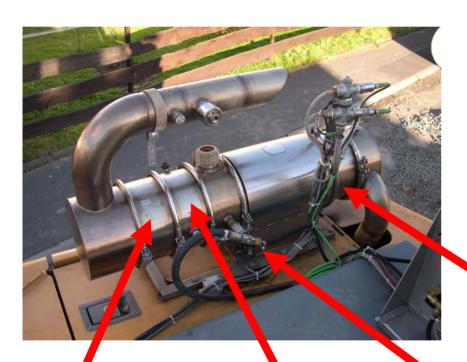
NO₂ CONVERSION VS DECOMPOSITION TEMPERATURE





LOW-NO₂ CRT® PROTOTYPE IN EXCAVATOR APPLICATION







NO₂ Decomposition
Catalyst Mixing section Diesel injection nozzle
Dr. Claus Görsmann: C

CRT®

Dr. Claus Görsmann: CATALYTIC COATINGS (Slide 42 of 62)

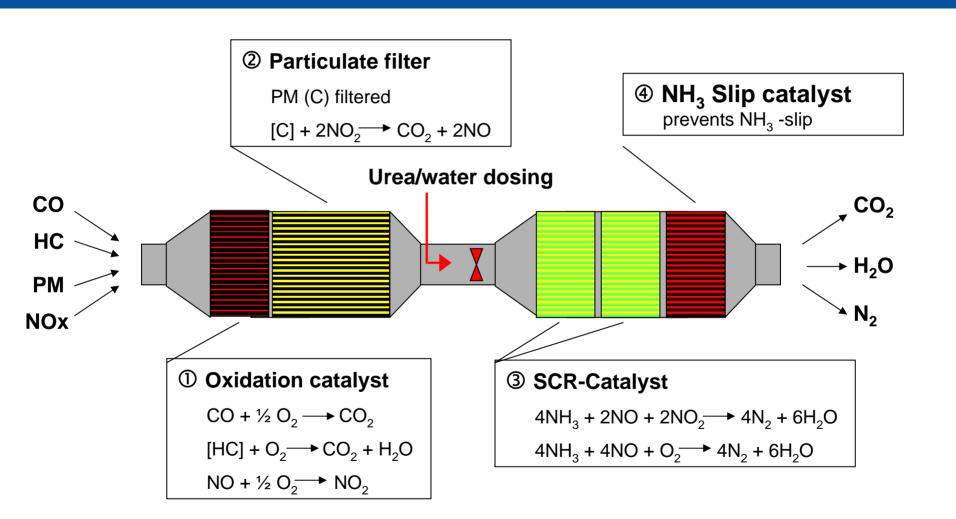
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SCRT® REACTIONS

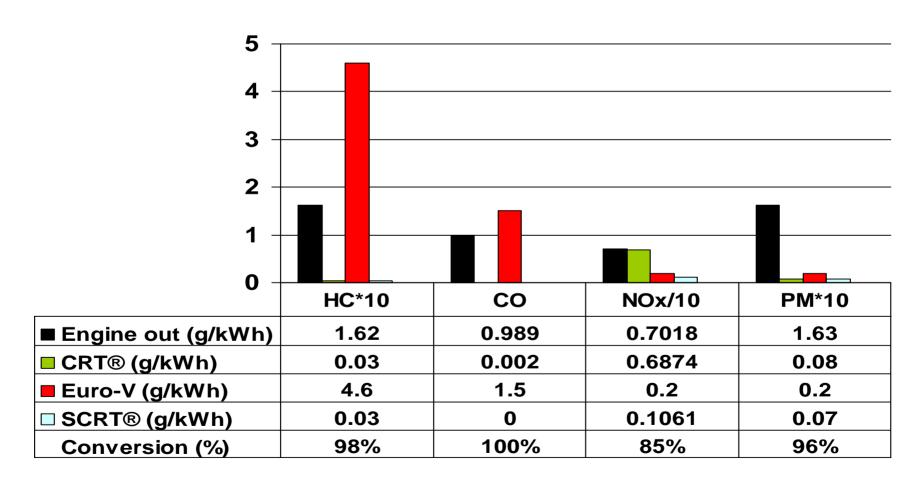




POLLUTANT REDUCTION FROM SCRT® -SYSTEM



EURO-I ENGINE, ESC



SCRT® SYSTEM NO₂ EMISSIONS



ESC Mode	Speed	Load	Temp. °C	Engine NO ₂ (ppm)	Tailpipe NO ₂ (ppm)
1	Low idle	0	140	22	3
2	low	100	397	20	8
3	Intermediate	50	325	27	3
4	intermediate	75	362	30	2
5	low	50	339	21	10
6	low	75	382	34	11
7	low	25	276	22	7
8	Intermediate	100	414	18	0
9	intermediate	25	287	22	3
10	high	100	478	16	0
11	high	25	295	19	0
12	high	75	363	20	0
13	high	50	323	20	0

Dr. Claus Görsmann: CATALYTIC COATINGS (Slide 46 of 62)

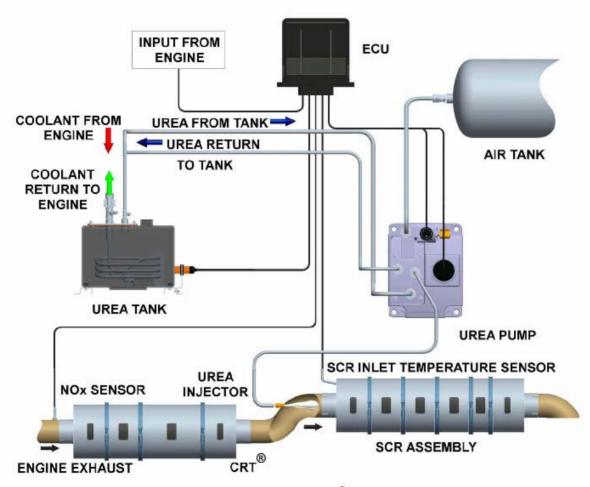
SCRT® SYSTEMS RETROFIT EXPERIENCE



- Currently there are around 100 Retrofit SCR and SCRT® systems installed in Europe and USA on various on-road and non-road applications.
- Typical in-field NOx daily conversions are in the range of 60-90%.
 - Meeting EU-V/EEV and Tier 4A emission targets has been demonstrated.

RETROFIT SCRT® SYSTEM SET-UP



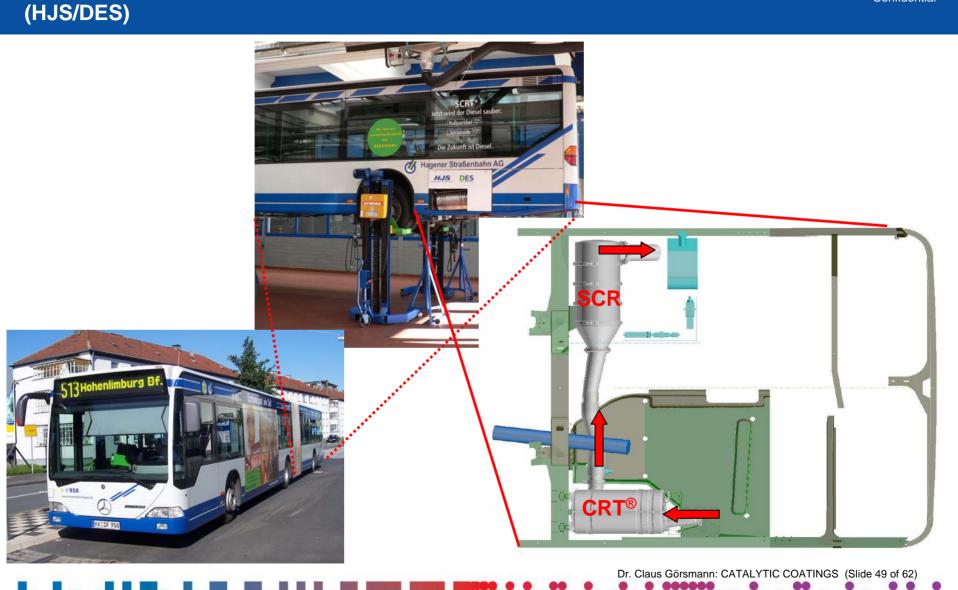


Johnson Matthey SCRT® Retrofit System

Dr. Claus Görsmann: CATALYTIC COATINGS (Slide 48 of 62)

RETROFIT SCRT® "50 SMF®" IN CITARO 0530 CITY BUS WITH OM 457 hLA EURO-III DAIMLERCHRYSLER ENGINE

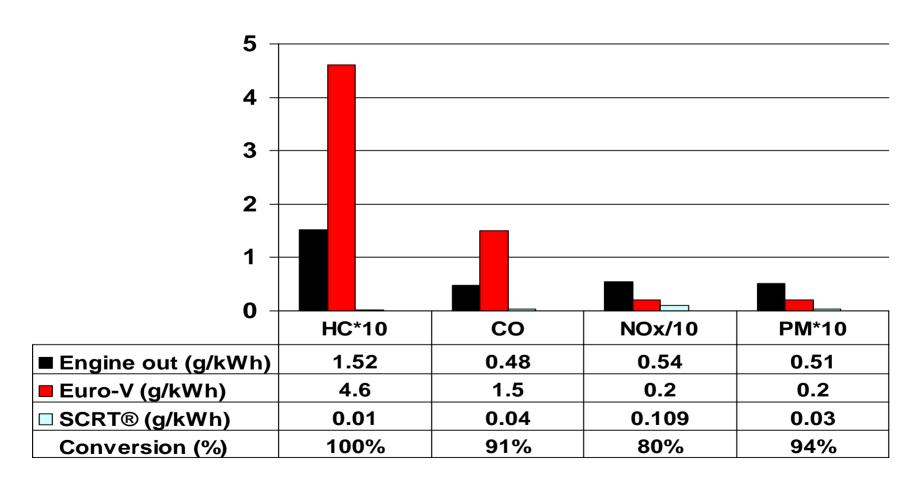




RETROFIT SCRT® SYSTEM ESC CYCLE EMISSIONS

(HJS/DES/TÜV-NORD)

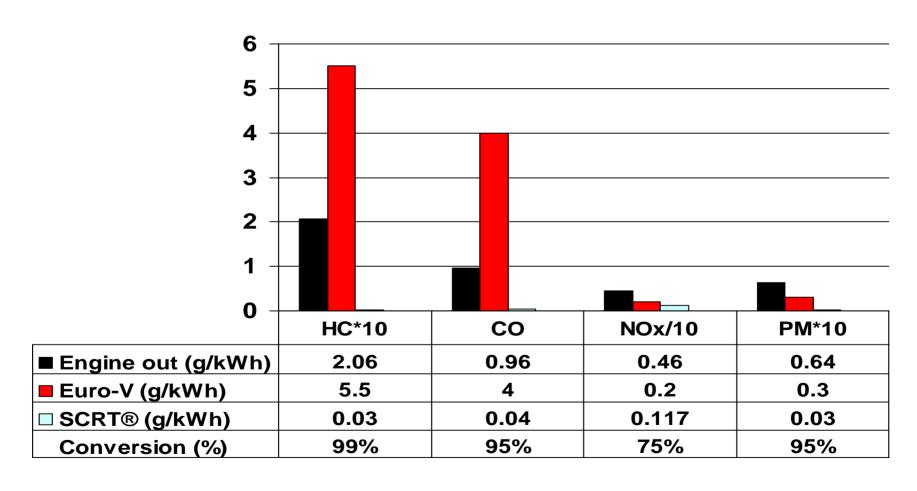




RETROFIT SCRT® SYSTEM ETC CYCLE EMISSIONS

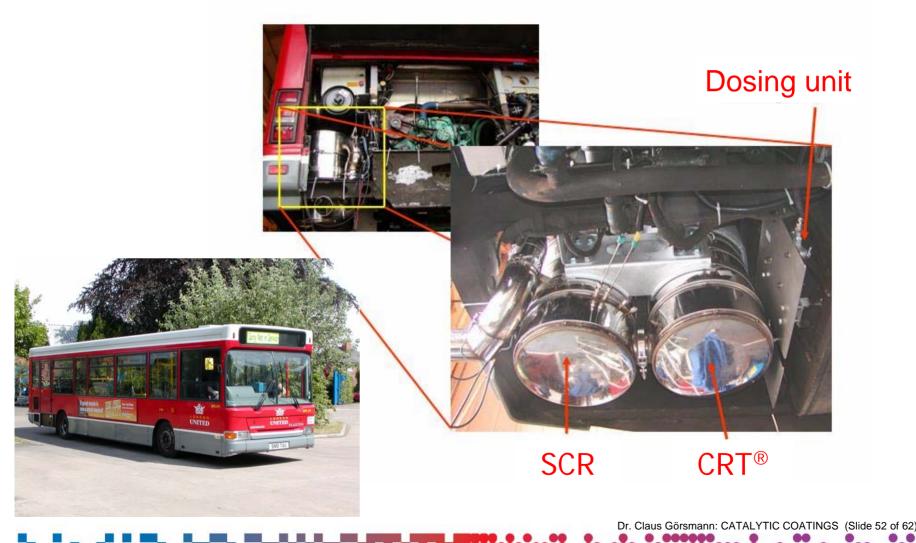
(HJS/DES/TÜV-NORD)





RETROFIT SCRT® SYSTEM IN DENNIS DART CITY BUS APPLICATION WITH CUMMINS 3.9-I ISB ENGINE (EMINOX)

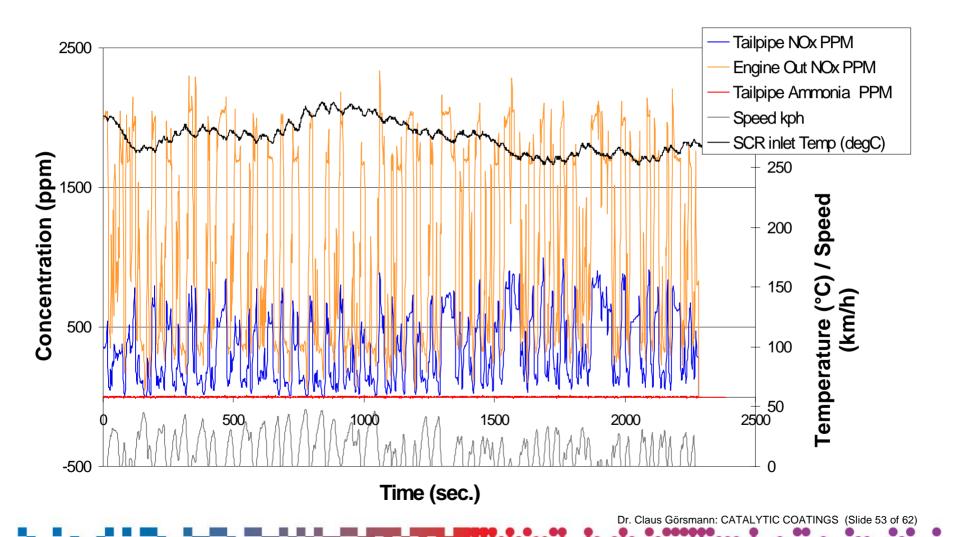




TYPICAL EMISSIONS FROM LONDON BUS FITTED WITH SCRT® (70% NO_x CONVERSION OVER MLTB CYCLE)



(EMINOX)



EXAMPLES OF ON-ROAD SCRT® SYSTEM APPLICATIONS IN NORTH AMERICA





Ralphs Grocery Truck



Long Beach Transit Bus



LA County Sanitation Trash Truck



BP Fuel Delivery Truck

Dr. Claus Görsmann: CATALYTIC COATINGS (Slide 54 of 62)

RETROFIT SCRT® APPLICATION EXAMPLE: BP FUEL DELIVERY TRUCK

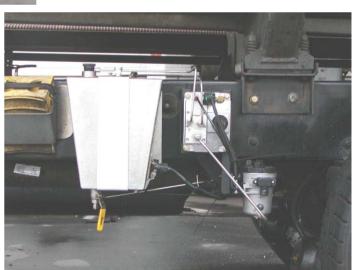






CRT Module

SCR Module



Dr. Claus Görsmann: CATALYTIC COATINGS (Slide 55 of 62)

RETROFIT SCRT® APPLICATION EXAMPLE: AIR COMPRESSOR

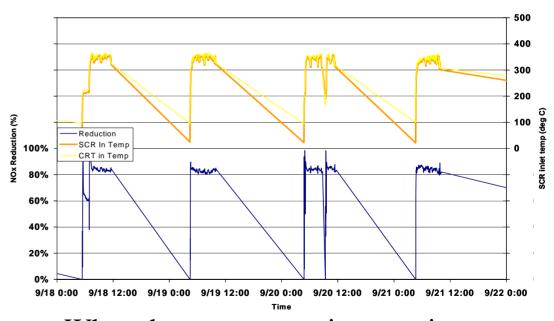






Real-time NOx conversion obtained on the Ingersoll Rand compressor with SCRT® over a four day period

NOX Reduction and SCR Inlet Temperature



When the compressor is operating The NOx conversion is over 80%.

Dr. Claus Görsmann: CATALYTIC COATINGS (Slide 56 of 62)

CONCLUSIONS SCRT®



- By combining CRT® and SCR systems SCRT® systems have been created, which effectively remove all four pollutants CO, HC, PM and NO_x from diesel exhaust emissions.
- With the reduction of NO_x not only NO₂ but also NO, which otherwise would oxidise in the atmosphere to NO₂, is effectively removed.
- Engine tests have demonstrated that Euro-V limits can be met.
- With engine independent SCRT® retrofit systems NO_x conversions above 70% are achieved in day to day operation.
- Retrofit SCRT® systems have proved being fit for use in day to day operation and are commercially available in Europe from Eminox Ltd. (GB) and DES Diesel Exhaust Systems GmbH (D) and in USA from Johnson Matthey Inc. (USA).

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CONCLUSIONS



- The vast majority of retrofit DPF systems utilise catalytic coatings in one or another way for DPF regenerations.
- Due to their simplicity, passive NO₂ based DPF systems are the most popular retrofit systems. These are well proven and have demonstrated high durability.
- Where the operating conditions do not allow the use of a passive system, active systems can be applied.
- Where not only PM but also NO₂ or NOx emissions need to be controlled, DPF systems can be combined with NO₂ decomposition or NOx reduction functions allowing the most complete pollutant reduction.

ACKNOWLEDGEMENTS



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- Peter Werth, Aurelie Nuribanel (JM Germany)
- Dr. Phil Blakeman (JM China)
- Steve Rawson, Nick Lyons, Helen Brewer, Martin Taylor (Eminox Ltd)
- Ingo Zirkwa, Sandra Arndt (HJS Fahrzeugtechnik GmbH & Co. KG)
- Thomas Vieth (DES Diesel Exhaust Systems GmbH)
- London United Busways Ltd, Transport for London, Hagener Straßenbahn AG

Dr. Claus Görsmann: CATALYTIC COATINGS (Slide 60 of 62)



Thank you for your attention!





Reserve slides



TECHNICAL TERMS AND ABBRIVATIONS (1 of 4)



- ACRTTM = Active regeneration CRT[®] (fuel injection + DOC + DPF/CSF)
- Cat = Catalyst
- CCRT[®] = Catalysed CRT[®] (DOC + CSF)
- CO = Carbon monoxide
- CO₂ = Carbon dioxide
- CRT® = Continuously Regenerating Trap (DOC + DPF)
- CSF = Catalysed soot filter (coated DPF)
- DOC = Diesel Oxidation Catalyst
- DPF= Diesel Particulate Filter
- ECU = Electronic Control Unit
- EEV = Environmentally Enhanced Vehicle

TECHNICAL TERMS AND ABBREVATIONS (2 of 4)



- EGR = Exhaust Gas Re-circulation
- EPA = Environmental Protection Agency
- EPA Tier 3, 4, 4A (4 interim), 4B (4 final) = US non-road emission legislation
- ESC = European Stationary Cycle
- EU Stage IIIA, IIIB, IV = European non-road emission legislation
- $H_2O = water$
- HC: Hydrocarbons
- HDD: Heavy Duty Diesel
- HDD US EPA2007 / ...2010 = US HDD on-road emission legislation valid from model year 2007 / 2010
- JM = Johnson Matthey

TECHNICAL TERMS AND ABBREVATIONS (3 of 4)



- kW = kilowatt
- L = litre
- NAC: NOx-Adsorber Catalyst
- NO = Nitrogen oxide
- NO₂ = Nitrogen dioxide
- NOx = sum of NO and NO $_2$
- NY DOS = New York Department of Sanitation
- O_2 = Oxygen
- OEM = Original Equipment Manufacturer
- OBD = On-Board Diagnostic
- P = Pressure
- PCRTTM = Partial CRT[®] (DOC + partial filter)

TECHNICAL TERMS AND ABBREVATIONS (4 of 4)



- PM = Particulate Matter
- ppm = parts per million
- s = seconds
- S = Sulfur
- SCR = Selective Catalytic Reduction
- SCRT® = DOC + DPF + SCR
- V = Vanadium

UREA-SCR



- Uses ammonia as reductant to remove NO_x
- Ammonia is usually obtained from an aqueous urea solution.
- Urea to ammonia:
 - NH₂C(O)NH₂ → HNCO + NH₃ (thermolysis at 120°C)
 - HNCO + $H_2O \rightarrow CO_2 + NH_3$ (hydrolysis at 160°C)
- SCR reactions with ammonia:
 - $4NH_3 + 4NO + O_2 \rightarrow 4N_2 + 6H_2O$ (fast reaction)
 - $2NH_3 + NO + NO_2 \rightarrow 2N_2 + 3H_2O$ (very fast r.)
 - $8NH_3 + 6NO_2 \rightarrow 7N_2 + 12H_2O$ (slow reaction)